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Preparation of monodisperse polystyrene particles using thiol-ended polyethylene oxide stabilizer in dispersion polymerization

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Summary

Radical dispersion polymerization of styrene in aqueous ethanol solutions was performed in the presence of a new reactive polyethylene oxide stabilizer with thiol end groups. This reactive stabilizer was compared to the more conventional poly (N-vinylpyrrolidone). Particles size distribution, molecular weights and kinetics were investigated. We demonstrate that the thiol ended dispersant displays a high stabilizing efficiency. Particles size, molecular weights and conversions are strongly influenced by the amount of stabilizer used.

Introduction

Recently, dispersion polymerization of styrene in aqueous ethanol solutions has been extensively studied because of the simplicity of the process for the preparation of micron size monodisperse polymer particles (1-7). This method involved the use of highly polar polymers such as poly (N-vinyl pyrrolidone), hydroxypropyl cellulose or poly (acrylic acid) as polymeric steric stabilizers. The stabilization was described to take place through hydrogen abstraction and grafting of the steric stabilizer to the particle surface (8-9). The graft copolymer, formed in situ can also be adsorbed onto the growing particles and stabilize them against coalescence. Both mechanisms are competitive and we still don't know which of them is dominant. Besides, there is no direct positive evidence in the litterature that the formation of a graft copolymer is essential for dispersion stability. This is probably the reason why, last ten years, an increasing interest was devoted to the use of suitable reactive stabilizers to get a more controlled stabilization. Among them, a new category of macromonomers has proved to be the most useful and efficient. Those are stabilizer precursors, based on polyethylene oxide of relatively low molecular weight, terminated at one end with a reactive acrylate or methacrylate ester group capable of further free radical polymerization (10-12).

The present paper describes our first results along this line using a transfer agent equivalent of macromonomer i.e an hydrophilic oligomer of polyethylene oxide carrying a thiol moiety at its end: POE_{113}-SH (I). This can be easily prepared from esterification of monomethylether of polyethylene oxide with thioglycolic acid as described in a previous paper (13).

$$CH_3\text{-}(O\text{-}CH_2\text{-}CH_2)_{113}\text{-}O\text{-}CO\text{-}CH_2\text{-}SH \qquad (I)$$

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Experimental

The dispersion polymerization of styrene (Aldrich: 5wt% based on 100 g of total reaction mixture) was carried out in a mixture of ethanol and water (Onyx: 95:5 v/v) by 2,2'-azobis (isobutyronitrile) (AIBN, Janssen Chemica: 2wt% based on monomer) at 70°C for 25 hours under nitrogen to give a stable dispersion system. Several amounts of POE_{113}-SH (Mw=5000 g/mol) were used and the new reactive stabilizer was compared to the more conventional poly (N-vinylpyrrolidone) (PVP K30: Aldrich, Mw=40000 g/mol) and to its precursor: POE_{113}-OH from Aldrich (Mw=5000 g/mol).

Samples of the dispersions were washed by centrifugation-redispersion cycles to remove excess stabilizer, monomer and initiator residues. The final particle size and size distribution were examined by transmission electron microscopy (TEM). Conversions were determined gravimetically. Size exclusion chromatographic analysis (SEC) was performed to measure the molecular weights and molecular weight distributions.

Results and discussion

Dispersion polymerization is generally carried out in the presence of a high polymer soluble in the reaction medium as stabilizer. Poly (N-vinylpyrrolidone) of intermediate molecular weight (PVP K30: Mw=40000 g/mol) has proved to be the best stabilizer. So, we have choosen it as a basis of comparison.

On the other hand, macromonomers of poly (2- oxazoline) were recently described as excellent stabilizers for dispersion polymerization of styrene (14). Compounds with moderate molecular weights (in between 3000 and 5000 g/mol) were shown to be more efficient than non-functionalized high molecular weights 2-oxazoline homopolymers (Mw≥50 000 g/mol). The concentration of macromonomer stabilizer necessary for preparation of monodisperse polymer particles was much lower than that of polymeric stabilizer in conventional dispersion polymerization.

This paper is dealt with functionalized polyethylene oxide carrying not a polymerizable chain end (as a macromonomer), but a powerfull transfer agent thiol group. In this paper, a comparison is made of the behaviour of such a macromonomer equivalent compound with the best conventional poly (N-vinylpyrrolidone) PVP K30.

Table 1 shows particle size (Dn), size distribution (Dw/Dn), molecular weight and molecular weight distribution (Mw/Mn) of polystyrene with respect to the nature and concentration of the stabilizer.

It is to be noted that the particle size and particle size distribution obtained by the POE-SH stabilizer was smaller than that by the usual PVP stabilizer (entry 1, 3). Moreover, polymerizations carried out with the POE-OH stabilizer resulted in massive coagulum (entry 2). These data indicate the high efficiency of the thiol ended reactive stabilizer to maintain the colloidal stability of the growing particles when compared to PVP or POE-OH. Concurrent with the size decrease, the weight average molecular weight increased with broadening in the molecular weight distribution. This is consistent with the inverse correlation between particle size and molecular weights usually reported in the litterature (15).

Table 1: Effect of the nature and concentration of stabilizer on particle size and molecular weight by dispersion polymerization.

Entry	Stabilizer	Stab. conc.[a]	Dn (nm)[b]	Dw/Dn[b]	Mw [c] (g/mol)	Mw/Mn	yield (%)
1	PVP	10	1930	1.09	23153	2.65	71
2	POE$_{113}$-OH	10		←	unstable	→	
3	POE$_{113}$-SH	10	311	1.03	41658	3.81	80
4	POE$_{113}$-SH	5	2052	1.1	28274	2.59	77
5	POE$_{113}$-SH	3	2280	1.02	23524	2.44	73

[a] Weight % for styrene
[b] As determined by TEM
[c] Weight-average molecular weight

In order to investigate the mechanism of monodisperse polystyrene particle formation in the present case, polymerization yield and particle size were measured. Figure 1 shows the time-polymer yield curve for the two kinds of stabilizers. The polymerization carried out in the presence of POE-SH proceeded faster than that with PVP.

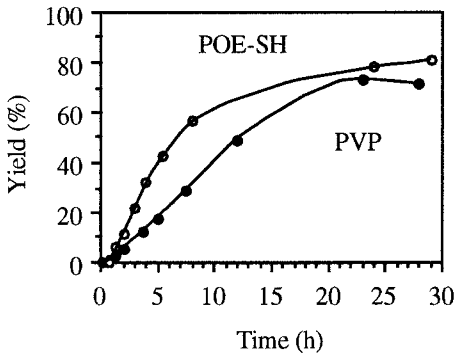

Figure 1: Time conversion curves of dispersion polymerizations for styrene in ethanol/water medium for PVP (•) and thiol-ended stabilizer (○).

In addition, Figure 2 shows that the volume of the resulting particles, calculated from the diameter of the particles as measured by dynamic light scattering, increased linearly with the polymer yield. Furthermore, the number of particles nucleated per liter of the dispersion was almost constant during the reaction. These data imply that the nucleation takes place at an early stage of the polymerization process followed by growth of the nuclei without formation of new particles to produce monodisperse polymer particles. A similar behaviour was also observed in the dispersion polymerization of styrene in the presence of PVP.

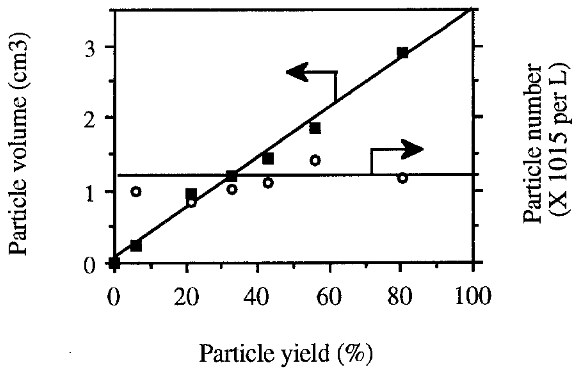

Figure 2: Particle yield versus particle volume and particle number. Dispersion polymerization of styrene was performed using 10 wt% of POE-SH (based on monomer).

On the basis of the above data, the following mechanism may be proposed. In the very early stage, polymerization proceeds homogeneously like solution polymerization. Afterwards, nucleation takes place and the grafted steric stabilizer is formed that control particles number. During the remainder of the reaction, particles grows as described elsewhere (2, 4) by two competiting mechanisms: 1- adsorption of monomer and subsequent particle phase polymerization leading to high molecular weights and 2- accretion of dead polymer formed by termination in the continuous phase (low molecular weights).

In the present case, using a thiol ended polyethylene oxide as reactive stabilizer, we believe that the reason for the increased conversion and molecular weight arises from the higher stabilizing efficiency of POE-SH when compared to PVP resulting in a greater number of stabilized nuclei, hence smaller final particles, which means the particles remain for a longer period in a regim of oligomer capture and solid phase polymerization. Stabilization may be attributed to extended alcoolo-soluble polyethylene oxide chains covalently bonded to the polymer in the latex particles by a grafting reaction between the polystyrene radicals and the thiol agent stabilizer. Works are now in progress to determine whether or not the reactive dispersant is chemically fixed on the polymer particles. Besides, NMR analysis is used to evaluate the amount of grafted stabilizer.

Further studies were carried out using various amounts of POE-SH. Results reported in Table 1 showed that the particle size increased by decreasing the concentration of the stabilizer (entry 3-5). So, the highest stabilizing efficiency (manifesting itself by the formation of small polymer particles) is exhibited by the stabilizer introduced in the greater amount. This is probably due again, to the larger number of stabilizing polymer molecules being able to stabilize a higher surface area and hence, produce smaller particles. This is in accord with the theories of particle formation proposed by Barret (8) and a similar phenomenon has been observed in the dispersion polymerization with PVP (8, 15-16). Once more, in accordance with the size increase, the weight average molecular weight decreased with narrowing in the molecular weight distribution while decreasing the stabilizer concentration .

Figure 3 shows the time conversion curves at different POE-SH concentrations.

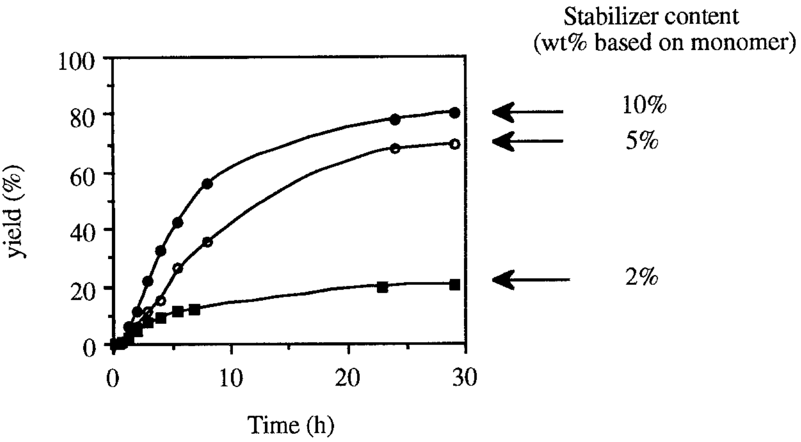

Figure 3: Time-conversion curves as a function of the amount of stabilizer.

The polymerization rate and final conversion are dependent on the stabilizer concentration. The increase in the rate of dispersion polymerization with increasing the concentration of the dispersant (i.e. with diminution of particles diameter) is more to be regarded as a result of the change in size of polymer particles than the ability of the stabilizer itself to influence directly the kinetics. If we assume that the main locus of polymerization is the polymer particles, we may consider that the mobility of the growing oligomers inside particles is considerably limited. As a consequence, the poorly mobile oligomer radicals are mostly adsorbed by the particles and do not diffuse inside them, but accumulate on their surface. The smaller is the total area of the particles, the greater is the possibility of termination of the oligomer radicals by recombination, which results in decrease in the rate of dispersion polymerization.

It is then to be concluded that the concentration of polyethylene oxide stabilizing chains is one of the parameters which control the particle size and stability of the latex as well as the polymerization rate and the final conversion.

As a conclusion, monodispersed polystyrene particles in the range of 300 to 2500 nm were obtained by dispersion polymerisation in polar media in the presence of a new reactive stabilizer carrying a thiol moity at its end. It is clear that the detailed mechanism by which latex particles are produced and stabilized cannot be deduced from the limited dara which have been obtained. However, we demonstrate that the final size, molecular weight and distributions are largely determined by the amount of stabilizer introduced and its ability to maintain the colloidal stability of the growing particles. It is then proved that stabilization is the determining factor which ultimately controls particles properties. Anchoring of the stabilizer into the particles was evidenced by NMR and responsible for the high stabilizing activity of the dispersant. NMR analysis are now in progress to determine the incorporation yield of the thiol-ended stabilizer.

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